Chemical and sulphur isotope compositions of pyrite in the Jaduguda U (–Cu–Fe) deposit, Singhbhum shear zone, eastern India: Implications for sulphide mineralization

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The Jaduguda U (–Cu–Fe) deposit in the Singhbhum shear zone has been the most productive uranium deposit in India. Pyrite occurs as disseminated grains or in sulphide stringers and veins in the ore zone. Veins, both concordant and discordant to the pervasive foliation, are mineralogically either simple comprising pyrite $\pm$ chalcopyrite or complex comprising pyrite + chalcopyrite + pentlandite + millerite. Nickel-sulphide minerals, though fairly common in concordant veins, are very rare in the discordant veins. Pyrite in Ni-sulphide association is commonly replaced by pentlandite at the grain boundary or along micro-cracks.

Based on concentrations of Co and Ni, pyrite is classified as: type-A – high Co (up to 30800 ppm), no/low Ni; type-B – moderate Co (up to 16500 ppm) and moderate to high Ni (up to 32700 ppm); type-C – no/low Co and high Ni (up to 43000 ppm); type-D – neither Co nor Ni. Textural and compositional data of pyrites suggest that the hydrothermal fluid responsible for pre-/early-shearing mineralization evolved from Co-rich to Ni-rich and the late-/post-shearing fluid was largely depleted in minor elements.

Sulphur isotope compositions of pyrite mostly furnish positive values ranging between -0.33 and 12.06% . Composite samples of pyrites with only type-A compositions and mixed samples of type-A and type-B are consistently positive. However, pyrite with mixed type-A and type-C and pyrite with type-D compositions have negative values but close to 0% . By integrating minor element and sulphur isotope compositions of pyrite in conjunction with other published data on the Jaduguda deposit, it is proposed that reduced sulphur for the precipitation of most pyrites (type-A, type-B) was likely derived from isotopically heavy modified seawater. However, some later sulphur might be magmatic in origin remobilized from existing sulphides in the mafic volcanic rocks in the shear zone.

1. Introduction

The Jaduguda U (–Cu–Fe) deposit, located at the central part of the Cu–U mineral district in the Singhbhum Shear Zone (SSZ), eastern India is economically the most important uranium deposit

that hosts the oldest and the deepest underground uranium mine in India. Besides uranium; Cu, Mo and Ni have previously been recovered and presently magnetite is being recovered as a by-product. Similar to other deposits in the SSZ, the Jaduguda deposit is hosted by strongly

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sheared, metamorphosed and hydrothermally-altered rocks. Although, most authors have advocated a hydrothermal origin for the deposits in the SSZ in general, major ore genetic models concerning the origin of polymetallic mineralization in the SSZ vary widely from magmatic-hydrothermal (Dunn and Dey 1942), to metamorphogenic related to migmatization (Banerji 1962; Talapatra 1968) to variants of volcanogenic massive sulphide deposits (VMS; Sarkar and Deb 1974; Sarkar 1984). Recently, Pal *et al* (2010) demonstrated multiple

events of hydrothermal fluid flux in the Jaduguda mineralized zone. Therefore, any ore genetic model should be assessed taking into account the multi-stage hydrothermal fluid flux and associated mineralization/mobilization.

This study aims at deciphering the stages of sulphide mineralization and their chemical evolution in relative time. Pyrite has widely been used to trace the physico-chemical evolution of sulphide deposit hosted in complexly deformed and metamorphosed rocks (Pal *et al* 2009 and

Figure 1. Regional geological map of the Eastern Indian craton showing the location of the Singhbhum shear zone and Jaduguda uranium deposit (redrawn from Saha 1994).

references therein). It is a common sulphide mineral in the sulphide ores of the Jaduguda deposit. In this paper, we integrate trace element and sulphur isotope compositions of pyrite of different morphologies and in different mineralogical associations to probe into the chemical evolution and probable source of hydrothermal fluid responsible for sulphide mineralization. We also briefly discuss the implications of these data and other available information on a probable ore-genetic model.

2. Geological background

The ~200 km long and ~1–5 km wide SSZ in eastern India occurs close to the boundary between the Archean cratonic nucleus with several volcano-sedimentary basins to its south, and the Proterozoic North Singhbhum Fold belt to its north

(figure 1). Two prominent basins, namely the Iron ore basin (Iron ore Group greenstone sequence) and the Dhanjori basin (Dhanjori Group of rocks) occupy the northwestern and southeastern parts of the cratonic nucleus, respectively. The fold belt, near the northern margin of the craton, is occupied by predominantly siliciclastic rocks of the Singhbhum Group. For a detailed discussion on the regional geology and age data, see Pal *et al* (2009) and references therein. The brittle–ductile SSZ (Ghosh and Sengupta 1987; Sengupta and Ghosh 1997) cuts across rocks of the Iron Ore Group, the Dhanjori Group and the Singhbhum Group. The rocks along the SSZ display prominent mylonitic foliation and conspicuous down-dip lineation. Progressive deformation resulted in folding of mylonitic foliation and development of tight isoclinal reclined folds (F1), which were superimposed by upright gently plunging asymmetric

Figure 2. Transverse section across the uranium ore lodes in Jaduguda hill showing the general rock types. Although the map shows the section up to a depth of 640 m, we have collected samples from depths up to 815 m level (compiled and modified from Gupta *et al* 2003; Srinivasan and Sarangi 1998).

folds (F2 and F3) with axial planar crenulation cleavage (Ghosh and Sengupta 1987; Sengupta and Ghosh 1997). The prograde metamorphism (M1) culminated in epidote-amphibolite facies accompanied the progressive deformation (Bandyopadhyay 2003; Sengupta *et al* 2005). The retrograde metamorphism (M2) exemplified by hydration of prograde assemblages postdated the progressive deformation.

All the uranium and copper mines occur in the stretch between Mohuldih to the west and Kanyaluka to the east. The Jaduguda uranium deposit is located in the central segment of the mineralized belt and at the northwestern fringe of the Dhanjori basin (figure 1). It occurs near the boundary between the volcano-sedimentary rocks of the Dhanjori Group and the predominantly siliciclastic rocks of the Singhbhum Group. Rocks of both these groups are exposed in the Jaduguda mine (figure 2). There are two mineable uranium lodes, referred to as the footwall- and the hanging wall lodes. In general, the footwall side of the footwall lode is represented by rocks belonging to the Dhanjori Group and the hanging wall side of the hanging wall lode is represented by rocks of the Singhbhum Group. The intervening zone is strongly mylonitic and might belong to upper Dhanjori. Three mutually planar structures, namely bedding planes, schistosity planes and shear planes are prominent in Jaduguda (Venkataraman *et al* 1971). Ore bodies are parallel to the schistose planes and the plunges of the ore shoots are parallel to the down-dip lineation defined by elongate minerals, mineral aggregates and stretched pebbles (Venkataraman *et al* 1971).

3. Sample location and methodology

In the Jaduguda mine, the sulphide lode occurs at the footwall side and overlaps the footwall uranium lode. Outside the sulphide lode, sulphide minerals are rare and mostly occur as disseminations. For this study, we collected 15 sulphide ($\pm$ uranium) ore samples from the sulphide lode from five different working levels (555, 620, 685, 750 and 815 m) and three samples from outside the sulphide lode at 555 m level; two from the footwall side and one from the hanging wall side. Samples from shallower levels could not be collected due to closure of mining at those levels.

All the samples were initially studied as hand specimens to determine the mode of occurrence of sulphide minerals, viz., disseminated *vs.* vein and concordant *vs.* discordant veins. Microtexture of pyrite from different associations is studied under standard transmitted and reflected light microscope from polished thin sections of the samples.

Ore minerals were identified integrating optical properties and chemical compositions.

Electron probe microanalyses of selected pyrite grains were conducted on a Cameca SX 100 instrument equipped with four wavelength dispersive spectrometers at the Geological Survey of India, Kolkata. All pyrites were analysed for Fe, S, Co, Ni, Cu, Pb and As. Pure sulphide and metals were used as standards. Each element was analysed for 10 s under 15 nA sample current and 20 kV accelerating voltage. The detection limits for trace elements are: Co, 500 ppm; Ni, 500 ppm; As, 1400 ppm; Pb, 2600 ppm.

For sulphur isotope studies, pyrite grains were either handpicked under a stereo microscope after grinding the samples or powders were collected directly from the sample using a mechanized hand-held Dremel rotary tool. Milling was done using a diamond bit. Samples of pyrite grains/powder were further ground to -200 mesh using an agate mortar. The sample capsules were combusted in a quartz tube reactor, pre-filled with WO_3 (+pure Cu) kept at 1050°C within a Flash HT 1112 elemental analyser, in the Stable Isotope National Facility Laboratory, Department of Geology and Geophysics, IIT Kharagpur. Purified SO_2 gas was introduced to a Delta Plus XP continuous flow mass spectrometer. The system was calibrated by analysing the NBS-123 sphalerite standard. Analytical precision was monitored by running both the NBS-123 and an internal BaSO_4 standard. The sulphur isotope compositions are expressed in terms of $\delta^{34}\text{S}$ (‰) relative to the Canyon Diablo Troilite standard. A routine precision of $\pm 0.2\%$ has been obtained for $\delta^{34}\text{S}$.

3.1 Host rock and mode of occurrences of pyrite

The sulphide lode is hosted in different rock types including chlorite schist, biotite schist, tourmaline-quartz schist and brecciated quartzite comprising variable proportions of quartz, chlorite, biotite and tourmaline. Other gangue minerals are albite, epidote, allanite, apatite and magnetite. The host rocks of the sulphide lode show evidence of intense shearing manifested by mylonitic foliation and lineation, S-C fabric and pressure fringe (*cf.* Mishra and Singh 2003). The mylonitic foliation is parallel to a set of pervasive schistosity defined by oriented grains of biotite and chlorite. Most pyrite in the sulphide lode occurs in the form of sulphide veins and stringers, either concordant or discordant to the pervasive schistosity and mylonitic foliation (figure 3). Pyrite outside the sulphide lode at the 555 m level occurs either as disseminated grains or as rare veins (figure 3). Samples, outside the sulphide lode, were collected from talc schist, banded

Figure 3. Hand specimen photographs of different pyrite-bearing samples. (a) Banded quartzite with disseminated fine-grained pyrite (not visible in the image. For pyrite photographs see figure 4). The sample is located at the hanging wall side of the hanging wall uranium lode at 555 m level. (b) Disseminated pyrite in talc schist. Pyrite grains are marked within the circle. (c) A concordant Fe-Cu sulphide vein. Note the lenticular habit of pyrite and quartz. (d) Part of an about 0.5-m wide concordant quartz-Fe-Cu sulphide vein. Note that the large quartz grains are elongated in habit. (e) A concordant Fe-Cu-Ni sulphide vein. Also note thin stringers paralleling foliation. (f) Discordant Fe-Cu sulphide vein in amphibolite outside the mineralized zone. The curved white lines show the orientation of sulphide minerals, presumably implying shear dragging. (g) Discordant Fe-sulphide (pyrite) vein. Note that the vein cuts across the mylonitic foliation defined by stretched quartz bands.

Figure 4. Reflected light photomicrographs, taken in plane polars, showing relevant ore textures. (a) Disseminated rounded fine-grained pyrite in banded quartzite. (b) Disseminated coarse-grained pyrite with Fe-Ti oxide inclusions in banded quartzite. (c) Disseminated euhedral pyrite in talc-chlorite schist. (d) Isolated pyrite, not in association with millerite/pentlandite in concordant Fe-Ni sulphide vein. (e) Pyrite replaced by pentlandite in concordant Fe-Cu-Ni sulphide vein. (f) Millerite replaced by pentlandite in concordant Fe-Cu-Ni sulphide vein. (g) Chalcopyrite partly replaces and surrounds pyrite in concordant Fe-Cu-Ni sulphide vein. (h) Pyrite replaced by somewhat more brownish pyrite (marked by arrow) in a concordant Fe-Cu sulphide vein.

quartzite and amphibolite. Amphibolite and talc schist occur at about 200 and 50 m on the footwall side of the footwall uranium lode, respectively and

the banded quartzite occurs at about 25 m on the hanging wall side of the hanging wall uranium lode. The talc schist comprises chlorite, talc, tremolite

and plagioclase; with variable proportions of magnetite, ilmenite and disseminated pyrite. Amphibolite occurs as small patches in biotite schist and comprises hornblende, albite, epidote, sphene, biotite and minor chlorite. This studied amphibolite, farthest from the sulphide lode, is less sheared compared to the host rocks of the sulphide lode and displays one set of poorly developed schistosity. A sulphide vein cuts across the foliation. The studied quartzite is typically banded with alternate Fe–Ti oxide-rich and quartz-rich bands and contains disseminated pyrite.

Based on the mode of occurrence, pyrite in Jaduguda deposit is classified as (a) disseminated pyrite and (b) vein pyrite. Classification of pyrite types based on texture and mineralogical association as discussed below is given in table 1.

3.1.1 Disseminated pyrite

Disseminated pyrite occurs in the banded quartzite and talc schist. Rounded to sub-rounded pyrite with diameters similar to the width of each band in banded quartzite occurs in association with Fe–Ti oxide (figure 4a). Additionally, large pyrite grains, locally with inclusions of Fe–Ti oxide, rare chalcopyrite and Ni-telluride occur in this rock (figure 4b). Pyrite, with rare chalcopyrite occurs as euhedral/subhedral grains in the talc schist and is commonly associated with chlorite (figure 4c). Rocks with disseminated pyrite generally contain abundant magnetite. Although disseminated pyrite also occurs in the sulphide lode, this textural type is minor compared to the sulphide veins and stringers.

3.1.2 Vein pyrite

Sulphide veins/stringers are abundant in the sulphide lode. Veins differ widely in thickness, ranging from 2–3 cm (rarely up to 100 s of centimetres) to about less than a millimetre. Veins and stringers in the sulphide lode are either concordant or discordant to the mutually parallel schistosity and mylonitic foliation in the host rock.

The concordant veins are commonly associated with quartz and in some places with magnetite. Large quartz grains are somewhat bulged at the centre and are tapering at the edges giving rise to lensoid shape probably arising as a result of ductile deformation (figure 3c). Pyrite in some of these veins also occurs as elongate grains paralleling foliation and in some others they occur as euhedral to subhedral grains (figure 4d, f). The host schist contains significant amount of magnetite in some cases.

The discordant veins in the sulphide lode cut across the schistosity and the mylonitic foliation

of the host rocks (figure 3g). Pyrite in these veins occurs as euhedral to subhedral grains and is locally fractured. Unlike the most discordant veins that clearly transgress the mylonitic foliation in the sulphide lode, the studied discordant vein in amphibolite is mineralogically complex and displays some sort of dragging of oriented sulphide minerals across the main foliation, presumably indicating shearing of sulphide minerals.

3.2 Mineralogical classification of veins

Both the concordant and discordant veins are mineralogically diverse. Along with pyrite, the veins contain one or more of the minerals such as chalcopyrite, pentlandite and millerite. Based on the association of Ni-sulphide minerals, the veins are classified as (a) Fe–Cu–Ni sulphide veins comprising pyrite+chalcopyrite+pentlandite+millerite±magnetite and (b) Fe±Cu sulphide veins comprising pyrite ± chalcopyrite ± magnetite (figure 3).

The concordant veins and stringers in the sulphide lode generally contain abundant Ni-sulphide minerals, except in a couple of samples. In the concordant Fe–Cu–Ni sulphide veins, pyrite occurs either as isolated grains (figure 4d) or in association with Ni-sulphide minerals. Pentlandite and millerite in the Ni-sulphide association commonly surround and replace pyrite along micro-cracks and grain boundaries implying their late paragenesis, compared to that of pyrite, in the veins (figure 4e). Pentlandite also replaces and surrounds millerite in these veins and stringers (figure 4f). Pyrite is locally surrounded and traversed by chalcopyrite (figure 4g). Pyrite in the concordant Fe + Cu sulphide vein and stringer with rare or no pentlandite is pervasively replaced along grain boundaries or micro-cracks by somewhat more brownish pyrite (figure 4h). Unlike the Fe–Cu–Ni sulphide veins, pyrites in these Fe + Cu sulphide veins are not replaced by Ni-sulphide minerals, although they are locally replaced by chalcopyrite. Minor pentlandite occurs as worm-like exsolved phases in chalcopyrite and as small irregular grains at the contact of chalcopyrite with silicate.

The discordant veins in the sulphide lode are generally poorer in Ni-sulphide minerals than the concordant veins. Pentlandite and millerite in the discordant sulphide vein in amphibolite commonly occur as minor exsolved phases either within chalcopyrite or at the place of contact of chalcopyrite with the host rock. Similar to concordant Fe–Cu sulphide veins, pyrite in this association has been partially replaced by chalcopyrite but not by any Ni-sulphide mineral. Although magnetite is present in some of the concordant veins, we have not observed magnetite in the discordant veins.

Table 1. *Summary of modes of occurrences and mineralogical associations of different pyrite and their broad compositions. (Refer to table 2 for representative compositions of pyrite.)*

Mode of occurrences	Ore mineralogy	Texture	Pyrite compositional type	Reference to serial no. in table 2
Disseminated	Pyrite + magnetite	Rounded fine-grained	Type-A core and rim	1, 2
		Coarse-grained locally with Fe-Ti oxide and Ni-tellurides	Type-A core and rim	3, 4
	Pyrite + magnetite	Euhedral to subhedral coarse-grained	Type-A core and rim	5, 6
	Pyrite + chalcopyrite + pentlandite $\pm$ millerite $\pm$ pyrrhotite $\pm$ magnetite	Isolated grains	Type-A core and rim type-A core and type-B rim	7, 8, 9, 10
Vein	Fe-Cu-Ni sulphide	Surrounded and replaced by chalcopyrite in Ni-sulphide association	Type-B core and rim	11, 12
		Surrounded and replaced by Ni-sulphide minerals	Type-B core and rim type-B core and type-C rim	13, 14, 15, 16
	Fe-Cu sulphide	Surrounded but not replaced by millerite	Type-A core and rim	17, 18
		Surrounded and replaced by chalcopyrite	Type-A core and rim	19, 20, 21, 22
Discordant	Pyrite + chalcopyrite + minor millerite (exsolved at the contact with silicate)	Replaced by optically different pyrite	Type-A replaced by type-C pyrite	23, 24
		Pyrite replaced and surrounded by chalcopyrite	Type-A core and rim	25, 26
	Fe-sulphide	Pyrite	Type-D	27, 28

3.3 Minor element compositions of pyrite

Major and trace element compositions were measured on 146 points in 118 representative pyrite grains of all morphological types and mineralogical associations. Overall, compositions deviate by <2% from the ideal 1:2 cation to anion ratio of stoichiometric pyrite and Co and Ni are detectable in most grains. There are large variations in the concentrations of Co and Ni in pyrite. These variations correlate well with different modes of occurrences (e.g., disseminated *vs.* vein) and mineralogical association of pyrite (Fe–Cu–Ni *vs.* Fe $\pm$ Cu sulphide vein). Accordingly, we have classified compositional types of pyrite based on their Co and Ni concentrations (figure 5). Representative compositions of different pyrite types are given in table 2.

Type-A: Pyrite with high Co and no/low Ni and Co:Ni ratios mostly varying between 100:1 and 10:1.

Type-B: Pyrite with moderate Co and Ni and Co:Ni ratios mostly straddling around 1:1 line.

Type-C: Pyrite with no/low Co and high Ni and Co:Ni ratios varying between 1:10 and 1:100.

Type-D: Pyrite with neither Co nor Ni.

3.4 Minor element compositions of different textural types

3.4.1 Disseminated pyrite

Disseminated pyrite in banded quartzite and talc schist are classified solely into the compositional group of high Co and low/no Ni type-A pyrite (figure 5, tables 1, 2). Disseminated type-A pyrite locally contains high arsenic (up to 0.8%), particularly those in the banded quartzite. Arsenic-rich type-A composition is locally noted in disseminated pyrite in the sulphide lode, where sulphide minerals occur mostly in the form of veins.

3.4.2 Vein pyrite

Unlike disseminated pyrite that represents only type-A composition, vein pyrite is compositionally diverse (figure 5, tables 1, 2). Nevertheless, some systematic patterns can be recognized in the compositions of pyrite from different veins and mineralogical associations. For example, although high Co and low/no Ni type-A pyrite is ubiquitous in all the concordant veins, type-B pyrites that contain moderate Co and Ni are present only in Ni-sulphide-bearing veins. Pyrites in Ni-sulphide-bearing veins are most diverse in composition.

Figure 5. Co and Ni concentrations and Co:Ni ratios of pyrite of different morphologies and in diverse mineralogical association. Co and Ni concentrations below detection limit are plotted with values of their corresponding detection limit. Horizontal and vertical dashed lines are detection limits. ■: disseminated pyrite; ○: concordant Fe–Cu–Ni sulphide vein, ▲: concordant Fe–Cu sulphide vein; ☆: discordant Fe $\pm$ Cu sulphide vein. The type-A field is defined based on compositions of disseminated pyrite, concordant Fe–Cu sulphide veins and isolated pyrite in Fe–Cu–Ni sulphide veins. Type-B field is defined by pyrite in association with Ni-sulphide minerals in Fe–Cu–Ni sulphide veins. Type-C field is defined by late pyrite in concordant Fe–Cu sulphide veins and some pyrite rims in Fe–Cu–Ni sulphide veins. Type-D is defined by discordant Fe-sulphide vein.

Table 2. *Compositions of representative pyrites of different morphology and in different mineralogical associations as described in table 1.*

Serial no.	Sample no.	S	Fe	Co	Ni	Cu	As	Pb	Total	Position	Pyrite type
1	JM-7 (C1)	52.86	46.02	1.20	bdl	bdl	bdl	bdl	100.25	Core	Type-A
2	JM-7 (C1)	52.56	46.37	1.06	bdl	bdl	bdl	bdl	100.19	Rim	Type-A
3	JM-7 (C4)	51.27	46.39	0.39	bdl	bdl	bdl	bdl	98.20	Core	Type-A
4	JM-7 (C4)	52.85	46.50	0.58	bdl	bdl	bdl	bdl	100.15	Rim	Type-A
5	JM-5 (C2)	51.72	45.20	2.10	bdl	bdl	0.80	bdl	100.06	Core	Type-A
6	JM-5 (C2)	52.79	45.74	1.43	bdl	bdl	0.40	bdl	100.57	Rim	Type-A
7	B-J-7 (C3)	52.41	44.11	3.06	0.06	bdl	0.78	bdl	100.47	Core	Type-A
8	B-J-7 (C3)	52.34	46.54	1.05	bdl	bdl	bdl	bdl	100.06	Rim	Type-A
9	B-J-10 (C3)	53.31	44.10	3.08	bdl	bdl	bdl	bdl	100.59	Core	Type-A
10	B-J-10 (C3)	53.03	45.24	0.60	0.63	bdl	0.17	bdl	99.83	Rim	Type-B
11	B-J-10 (C4)	51.35	43.33	1.65	3.27	bdl	bdl	bdl	99.90	Core	Type-B
12	B-J-10 (C4)	53.74	45.85	1.23	0.39	bdl	bdl	bdl	101.66	Rim	Type-B
13	B-J-10 (C3)	52.32	45.18	0.44	0.96	bdl	bdl	1.72	100.62	Core	Type-B
14	B-J-10 (C3)	53.24	45.50	0.52	1.77	bdl	bdl	bdl	101.14	Rim	Type-B
15	B-J-6 (C1)	52.68	44.91	1.10	1.02	bdl	bdl	bdl	99.88	Core	Type-B
16	B-J-6 (C1)	53.16	43.28	0.06	3.78	bdl	bdl	bdl	100.40	Rim	Type-C
17	B-J-7 (C2)	52.13	45.29	2.09	bdl	bdl	bdl	bdl	99.63	Core	Type-A
18	B-J-7 (C2)	52.50	44.86	2.23	0.11	bdl	bdl	bdl	99.82	Rim	Type-A
19	JM-685-5-1	51.85	46.52	0.74	0.09	bdl	bdl	bdl	99.41	Core	Type-A
20	JM-685-5-1	52.18	46.09	1.05	0.08	bdl	bdl	bdl	99.59	Rim	Type-A
21	JM-14-5	53.00	46.02	1.04	bdl	bdl	bdl	bdl	100.36	Core	Type-A
22	JM-14-5	52.79	44.73	1.78	0.05	bdl	bdl	bdl	99.58	Rim	Type-A
23	JM-13a-3	53.15	46.40	0.63	0.1	bdl	bdl	bdl	100.45	Replaced by pyrite of analysis no. 24	Type-A
24	JM-13a-3	52.52	42.93	0.03	4.3	bdl	bdl	bdl	99.84	Replaces pyrite of analysis no. 23	Type-C
25	JM vein	53.07	46.59	0.47	0.07	bdl	bdl	bdl	100.52	Core	Type-A
26	JM vein	51.80	45.62	1.64	0.07	bdl	bdl	bdl	99.34	Rim	Type-A
27	B-J-8	52.76	47.05	bdl	bdl	bdl	bdl	bdl	99.94	Core	Type-D
28	B-J-8	52.45	47.25	bdl	bdl	bdl	bdl	bdl	99.89	Rim	Type-D

Isolated pyrites, not associated with Ni-sulphide minerals, are commonly type-A and rarely type-B in composition, both at the core and rim. In contrast, pyrite displays complex compositional patterns when it is intimately associated with and at places replaced by Ni-sulphide minerals. For example, while in some grains both core and rim are type-B with moderate Co and Ni concentration, in some grains the core is type-A with high Co and no/low Ni and the rim is type-B or the core is type-B and the rim is type-C with no/low Co and high Ni. When chalcopyrite replaces pyrite, although both core and rim are type-B, there seems to be significant depletion in Ni concentration at the rim of pyrite with a corresponding rise of the same in chalcopyrite. Most pyrites are type-A in composition both at the core and at the rim in concordant Fe–Cu sulphide veins, with minor or no Ni-sulphide minerals. However, in such veins, early type-A pyrite is replaced by type-C pyrite, the latter also occurs as micro-veins in the former. Type-D pyrite with neither Co nor Ni is very rare in

Fe–Cu–Ni and Fe–Cu sulphide veins and only locally found at the rim of type-A or type-B pyrites.

Similar to concordant Fe–Cu sulphide veins, the discordant vein (that occurs outside the mineralized zone in the amphibolite) is also represented by type-A pyrite. The discordant pyrite vein in the mineralized zone is represented by only type-D compositions.

3.5 Sulphur isotope compositions

The $\delta^{34}\text{S}$ values of different pyrite types are presented in figure 6. Sulphur isotope compositions of two composite samples of disseminated type-A pyrite are positive, the highest value of +12.06‰ is obtained in the banded quartzite. We could not separately sample pyrite of different compositions (A, B and C) from the Ni-sulphide-bearing concordant veins, as they are intricately associated. However, the $\delta^{34}\text{S}$ values of eight mixed pyrites in

Figure 6. Sulphur isotope compositions of different pyrites.

these veins are all positive ranging between +0.12 and +4.70‰. Two composite samples of concordant Fe–Cu sulphide veins display values of –0.01 and +2.40‰, the lower value is from a sample where type-A pyrite is replaced by type-C pyrite and the higher value in the sample is represented solely by type-A composition. Amongst the discordant veins, the lowest $\delta^{34}\text{S}$ value is shown by the type-D pyrite vein without any other associated sulphide. Two samples of composite type-A pyrite from the discordant Fe–Cu sulphide vein in amphibolites display positive values of +1.06 and +2.28‰.

Sulphur isotope compositions of pyrite are thus mostly positive. Composite samples of pyrites with only type-A compositions and mixed samples of type-A and type-B are consistently positive. However, pyrite with mixed type-A and type-C and pyrite with type-D compositions are somewhat negative but close to 0‰.

4. Discussion

4.1 Events of mineralization and evolution of mineralizing fluid

Occurrences of sulphide minerals in morphologically and mineralogically diverse veins in the same locale are footprints of multiple events of sulphide formation in the Jaduguda deposit. The concordant sulphide veins and stringers parallel to the mylonitic foliation/schistosity and commonly with stretched pyrite and lenticular quartz must have formed prior to the closing of shearing. However, since all the prominent planar structures are parallel to each other (*cf.* Venkataraman *et al* 1971), we cannot uniquely place the concordant veins in

relation to the development and evolution of each fabric. We therefore classify these sulphide veins broadly as pre-/early-shearing veins. Similarly, sulphide veins, discordant to the mylonitic foliation must have formed either towards the end stage or postdating shearing and are thus classified as late-/post-shearing. The abundance of Ni-sulphide minerals in most concordant veins and rarity of these minerals in discordant veins in tandem with ubiquitous presence of Co-/Ni-rich pyrite (type A and B) in the former imply that the main event of Ni and Co addition in the mineralized rock was pre-/early-shearing. Additionally (a) presence of magnetite in some concordant veins and their absence in the discordant veins and (b) common occurrences of magnetite $\pm$ sulphide vein paralleling and locally folded with the foliation (Das 2009) suggests that Fe is also likely to have been added during this period.

Mineralogical diversity of the concordant veins and compositional variations of pyrite collectively implies that the trace element compositions and hence chemical characters of the ore-forming hydrothermal fluid varied during the event of pre-/early-shearing mineralization. We have not observed any cross-cutting relations between Fe–Cu and Fe–Cu–Ni sulphide-bearing concordant veins that could physically demonstrate their relative timing of formation. However, the micro-textures and compositions of pyrite in the veins from the sulphide lode provide clues to the changing fluid composition. For example, (a) replacement of type-A pyrite by Ni-sulphide minerals and corresponding compositional modification of type-A to type-B close to the zone of replacement, (b) type-A core and type-B/type-C rim of single pyrite grain in Fe–Cu–Ni sulphide vein, and (c) replacement and fracture filling of Co-rich type-A pyrite by Ni-rich type-C pyrite in the concordant Fe–Cu sulphide vein collectively indicate that the fluid composition changed from relatively Co-rich to Ni-rich. The concentration of Ni of this later fluid might have been so high at places that it led to the crystallization of Ni-phases (millerite/pentlandite) as well as resulted in Ni-enrichment of existing pyrite and perhaps precipitation of new Ni (plus Co)-rich pyrite (type-B). A variant of this fluid or a different fluid might have been incapable of precipitating Ni-bearing phases and incorporated Ni as trace elements alone in pyrite, making its concentration very high in these pyrites (type-C replacing type-A in concordant Fe–Cu sulphide vein).

The discordant sulphide vein with minor Ni-sulphide minerals and type-A Co-rich pyrite perhaps marks the end stage of Co–Ni addition to the rock. Minor shear-dragging of sulphide minerals in this vein likely indicates that the vein formed prior to the closing of shearing but after the formation of

the discordant veins in a relatively brittle regime. The final stage of fluid evolution is represented by discordant pyrite vein, cross-cutting mylonitic foliation/schistosity with distinctly euhedral grains of type-D composition.

The Co and Ni concentrations of pyrite reflect the concentrations of these elements in the hydrothermal fluid from which pyrite precipitated. Hydrothermal concentrations depend on the availability at the source/country rock and solubility of the elements in the fluid, the latter is a function of P , T and composition of the fluid. We cannot confirm whether the source/country rock was gradually depleted in Co and Ni or the latter fluids were not capable of transporting significant concentrations of these elements. However, the textures and compositions of pyrite from the main ore zone indicate that the fluid related to pre-/early-shearing broadly evolved from Co-rich to Ni-rich and the late-/post-shearing fluid was largely depleted in these elements. Similar evolutionary history of hydrothermal fluid precipitating Co-rich and Ni-depleted pyrite followed by precipitation of moderately Co and Ni-rich pyrite has been demonstrated from Turamdih uranium deposit in the Singhbhum shear zone (Pal *et al* 2009).

4.2 Source of sulphur and the hydrothermal fluid

The sulphur isotopic composition of pyrite is a function of T , fO_2 and pH besides the isotopic composition of the fluid. Based only on the $\delta^{34}S$ values of pyrite, we therefore cannot uniquely assign the source of hydrothermal fluid responsible for the precipitation of different generations of pyrite. However, consistent positive $\delta^{34}S$ values of minor element rich pre-/early-shearing type-A, type-B and mixed type-A and type-B pyrite, the highest being 12.06‰, indicate that the reduced sulphur was immediately or ultimately derived from an isotopically heavy fluid. Boron isotope compositions of pre-shearing tourmaline from the ore zone at Jaduguda indicate a strong seawater component for the contained boron (Pal *et al* 2010). Locally, the very high tourmaline content of these rocks further implies that the most likely source was basinal brine/evaporite. It therefore stands to reason that sulphur for the pre-/early-shearing sulphide was likely derived from seawater or modified seawater including basinal brine or even evaporite-derived fluid. The presence of (a) high salinity fluid inclusion in the mineralized zone (Mishra and Singh 2003), (b) Cl-rich biotite and amphibole in mineralized and altered rocks (Das 2009), (c) Cl-rich scapolite in alteration zone (Das 2009), and (d) abundant tourmaline in the ore zone collectively imply that the hydrothermal

fluid responsible for pre-/early-shearing alteration-mineralization was likely a high salinity brine. Additionally, high trace element concentration particularly that of Co, seems to be the characteristic of deposits where involvement of high salinity fluid has been unequivocally demonstrated (Mazdab 2001; Mazdab and Barton 2001). Integrating all available information, the source of sulphur for disseminated pyrite and pyrite in concordant veins is best assigned to basinal brine or marine evaporite-derived fluid.

The type-D pyrites or the pyrites found in the discordant veins have sulphur isotopic values either close to zero or are slightly negative. $\delta^{34}S$ values close to zero can possibly be explained by derivation of sulphur from magmatic source (mobilized from magmatic rock or derived from magmatic-hydrothermal fluid), or they could have been remobilized from existing sulphide minerals in mafic volcanics. However, cogenetic felsic igneous rock, capable of providing magmatic-hydrothermal fluid, has not yet been unequivocally demonstrated from the deposit. Thus, given the present understanding on the Jaduguda deposit, we suggest that this sulphur might constitute the redistributed sulphur from existing sulphide minerals in mafic magmatic rock in the shear zone.

4.3 Deposit type

Trace element concentrations of pyrite have long been used to decipher the process of sulphide formation and the deposit type. Pyrite precipitated from high temperature hydrothermal solutions in volcanogenic massive sulphide deposits and Fe oxide Cu–Au deposits (Loftus-Hills and Solomon 1967; Price 1972; Bralía *et al* 1979; Mookherjee and Philip 1979; Green *et al* 1981; Bajwah *et al* 1987; Raymond 1996; Clark *et al* 2004; Mazdab 2001; Mazdab and Barton 2001) seems to contain high concentrations of trace elements. However, volcanogenic massive sulphide deposits worldwide seem to have much lower concentration of Co (usually <5000ppm; Bajwah *et al* 1987) compared to those in Fe oxide (Cu–Au) (IOCG) deposit that might contain up to 40000 ppm Co (Mazdab 2001; Mazdab and Barton 2001). It is emphasized that trace element concentrations of pyrite alone cannot unequivocally settle the issue of type of deposit. The high minor element concentrations of pre-/early-shearing pyrite; inferred source and nature of hydrothermal fluid based on this study and other published data; typical metal association of U, Cu, Fe, REE (in monazite and allanite); and abundant magnetite (magnetite is being recovered as by-product from the Jaduguda deposit), are similar to the characteristics of

many Fe-oxide copper-gold (IOCG) deposits in the world (Hitzman *et al* 1992; Barton and Johnson 1996, 2000; Williams *et al* 2005). However, there might be alternative interpretations and models including superimposition of different deposit types in the same location. A detailed study on alteration types and pattern vis-à-vis ore mineralization, mineralogy and mineral chemistry and lithotectonic ambience is necessary to conclude this proposition.

5. Conclusions

This study indicates that the Jaduguda U (Cu–Fe) deposits witnessed recurrent events of hydrothermal sulphide mineralization over a prolonged period of time. Sulphide mineralization may be classified as pre-/early-shearing and late-/post-shearing. Most ore metals (Cu, Fe, Ni, Co) were added to the mineralized rock during the early history of the shear zone evolution. The mineralizing fluid related to pre-/early-shearing pyrite evolved from Co-rich to Ni-rich composition. The latest fluid that postdated most of shearing did not add much of Co and Ni, particularly Ni, into the deposit as indicated by Co/Ni-poor/depleted pyrite and absence/rarity of Ni-sulphide minerals. Trace element and sulphur isotope compositions of pyrite in conjunction with other published data indicate that modified seawater, presumably basinal brine or evaporite-derived fluid, was likely involved in most sulphide mineralization. The known geological and geochemical data and data presented in this contribution are similar to the IOCG-type mineralization in the Jaduguda deposit and demands a rigorous study to understand the mineralization in Jaduguda, in particular and in the SSZ, in general.

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